

**Amendments to the Drawings:**

The attached sheet of drawings includes changes to FIG. 1. This sheet replaces the original sheet containing FIG. 1. In FIG. 1, the previously omitted reference numeral 10 and the previously omitted legend "Prior Art" have been added.

Attachments: Replacement Sheet

Annotated Sheet Showing Changes

## **REMARKS/ARGUMENTS**

Applicants respectfully request reconsideration of this application in view of the foregoing amendments to the claims and the following comments. The Office Action mailed June 16, 2005, raised several matters, which Applicants discuss in order below.

### **Restriction Requirement**

On pages 2 and 3 of the Office Action, the Examiner restated his prior issuance of a restriction requirement, restricting this application to one of two identified inventions:

- I. Claims 1-24, drawn to a photomask assembly;
- II. Claims 25-55, drawn to various alternative methods for making a photomask assembly.

Applicants hereby confirm the prior election of the invention of Group I. Claims 25-55, drawn to the invention of Group II, have now been canceled, without prejudice. Applicants intend to pursue protection for the invention of Group II in a divisional patent application.

### **Objection to Drawings**

On pages 3 and 4 of the Office Action, the Examiner objected to the drawings, because FIG. 1 lacked a reference numeral 10 and lacked a legend "Prior Art."

By this Amendment, Applicants submit a replacement sheet containing a corrected FIG. 1. In view of this submission, the objection to the drawings should now be withdrawn.

### **Objection to the Specification**

On pages 4 and 5 of the Office Action, the Examiner objected to the specification, because paragraph [0039], line 9, recited the phrase "with a difference of  $\pm 20\%$ , which the Examiner asserted should have been "within a difference of  $\pm 20\%$ ."

By this Amendment, Applicants have amended the specification to correct the error noted by the Examiner. In view of this correction, the objection to the specification should now be withdrawn.

### **Rejection of Claims 1-24 Under 35 U.S.C. § 112**

#### **35 U.S.C. § 112, First Paragraph**

On page 5 of the Office Action, all of claims 1-24 were rejected under 35 U.S.C. § 112, first paragraph, as allegedly failing to comply with the enablement requirement. Specifically, the Examiner asserted that the units recited for gas permeability to oxygen or nitrogen, i.e., “ml.mm/cm<sup>2</sup>.min.MPa,” are not comparable to those typically used for permeability, which the Examiner asserted to be cm<sup>3</sup>/sec/cm<sup>2</sup>. Applicants respectfully disagree and therefore traverse this rejection.

The units used by Applicants to characterize gas permeability are, in fact, commonly used in the field. The units, ml.mm/cm<sup>2</sup>.min.MPa, have dimensions of L<sup>3</sup>.L/(L<sup>2</sup>.t.P), where L is length (or spatial dimension), t is time, and P is pressure. These units alternatively can be expressed as L<sup>2</sup>/(t.P), or L<sup>3</sup>/(L.t.P).

As support for Applicants’ use of the units “ml.mm/cm<sup>2</sup>.min.MPa” to designate gas permeability, Applicants direct the Examiner’s attention to the authoritative publications identified below. Copies of these publications are enclosed for the Examiner’s convenient reference. All of these publications characterize gas permeability using units analogous to those used by Applicants.

- Brandrup, J. et al., Polymer Handbook, Fourth Edition, John Wiley & Sons, Inc. New York, New York, 1999, pages VI/543–VI/569. (See pages VI/544 and VI/545).
- Koros, W.J. et al., “Membrane-Based Gas Separation, Journal of Membrane Science, 83, Elsevier Science Publishers B.V., Amsterdam, 1993.

- “Standard Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting,” ASTM International Standard D 1434-82, ASTM International, 2004.

In making this rejection, the Examiner asserted that the units typically used for permeability of a porous article specify “volume per unit of time per cross-sectional area of the porous article, such as --  $\text{cm}^3/\text{sec}/\text{cm}^2$  -- (which can alternatively be expressed as --  $\text{cm}^3/(\text{sec}.\text{cm}^2)$  --.” Applicants respectfully disagree. The units asserted by the Examiner, which have dimensions of  $\text{L}^3/(\text{t}.\text{L}^2)$ , or alternatively  $\text{L}/\text{t}$ , actually correspond to those used for a parameter commonly referred to as “face velocity,” “volumetric rate of flow per unit face area,” “transmission rate,” or “flux.” This parameter corresponds to fluid flow rate through a unit area of a surface of a porous solid.

The above-identified publications support the notion that these units apply to “transmission rate” or “flux,” but not gas permeability. See, *Brandrup et al.*, at page VI/544, and *Koros et al.*, at page 16. For the correct definition of gas permeability, Applicants direct the Examiner’s attention to *Brandrup et al.*, page VI/543, and *Koros et al.*, page 16 (Eq. 2). Moreover, Applicants note that the Examiner failed to cite even a single reference as supporting his assertion regarding the proper units for gas permeability.

For these reasons, the Examiner’s rejection of claims 1-24 under 35 U.S.C. § 112, first paragraph, should be withdrawn.

### **35 U.S.C. § 112, Second Paragraph**

On pages 5 and 6 of the Office Action, claims 21 and 22 were rejected under 35 U.S.C. § 112, second paragraph, as allegedly indefinite. Specifically, the Examiner asserted that the phrase “scavenge *certain* chemicals” is indefinite. The Examiner suggested that this rejection could be overcome by amending the phrase to “scavenge *harmful* chemicals.” By this Amendment, Applicants have amended claims 21 and 22 to substitute the term “harmful” for “certain,” as the Examiner suggested be done. In view of these Amendments, this § 112 rejection of claims 21 and 22 should now be withdrawn.

### Rejection of Claims 1-24 Under 35 U.S.C. § 103(a)

On pages 6 and 7 of the Office Action, independent claim 1 and its dependent claims 2-24 all were rejected under 35 U.S.C. 103(a), as allegedly obvious over U.S. Patent No. 6,507,390 to Ivaldi (the “Ivaldi patent”) in view of U.S. Patent Application Publication No. 2003/0035222 to Okada et al. (the “Okada publication”). Applicants respectfully traverse this rejection for the reasons set forth below.

In making the § 103(a) rejection, the Examiner presented the following comments regarding the Ivaldi patent and the Okada publication:

Ivaldi teaches an apparatus mask assembly having a porous metal frame 206 (made from sintered metal particles having pores sized from sub-micron to plural microns each, as controlled by sintering) between a reticle (mask) 104 and a glass pellicle 108 (col. 5 lines 5-31).

Ivaldi does not specifically teach the other limitations of instant claims 1-24.

Okada et al. teach a pellicle having a frame made of porous quartz glass (abstract, paragraph [0014]). The frame can be made of other similar material to have a coefficient of thermal expansion (CTE) within  $\pm 50\%$  of that for the adjacent pellicle (if not quartz glass). The CTE for quartz glass is  $1 \times 10^{-7}/^{\circ}\text{C}$  to  $40 \times 10^{-7}/^{\circ}\text{C}$  [0046] (which converts to a CTE of 0.1 ppm/ $^{\circ}\text{C}$  to 4 ppm/ $^{\circ}\text{C}$ , reading on the instant range of CTE of 0.01-10 ppm/ $^{\circ}\text{C}$  and  $\pm 50\%$  and encompassing the instant narrower CTE ranges within  $\pm 20\%$ ).

It would have been obvious to one of ordinary skill in the art at the time of the invention to have used a porous silica or quartz glass frame having a lower CTE as taught by Okada et al. in the photomask assembly taught by Ivaldi in order to obtain a better match of CTE between the frame and mask or pellicle. A porous silica or quartz glass frame would

be expected to inherently possess the various properties recited by the instant claims.

Office Action mailed June 16, 2005, pages 6-7.

Applicants respectfully disagree with the Examiner's assertions regarding the teachings of the Ivaldi patent and Okada publication. Both references fail to disclose important aspects of Applicants' claimed invention. Even if the teachings of these two references were to be combined in the manner the Examiner suggests, the resulting combination still would fall short of Applicants' claimed invention.

The Ivaldi patent discloses a photolithography system incorporating a metal pellicle frame 206 having sufficient porosity to allow gas to pass through it and thereby equalize the pressure in the air gap 112 beneath the pellicle 108 with atmospheric pressure. This porosity is said to eliminate distortion to the reticle 104 and/or the pellicle 108. Regarding the pellicle frame 206 and its porosity, the patent states as follows:

In a preferred embodiment, porous frame 206 is manufactured from one or more metals. For example, porous frame 206 may comprise iron, copper, bronze, nickel, titanium, or other metal, or any combination or alloy thereof. Porous frame 206 comprises pores formed in the metal(s) by a pore forming process. For example, porous frame 206 may be made from metal powder particles or filaments bonded at their contact points by sintering, which may create a continuous, well-defined network of pores between the particles or filaments. Sintering techniques generally weld together and grow a contact area between two or more initially distinct particles at temperatures below the melting point. Other processes for forming pores are also within the scope of the present invention. The porosity, or pore size, may be controlled by the production process, and may be determined on an application-by-application basis. For example,

the porosity may be specified in microns, or in fractions of a micron. The invention, however, is not limited to these porosity values. . . .

Ivaldi patent, column 5, lines 5-23.

The Ivaldi patent fails to provide any significant guidance regarding the frame's desired porosity, pore size, or gas permeability. In fact, the patentee fails to evince any recognition at all that he even understands the difference between these parameters; for example, he seems to use the terms "porosity" and "pore size" interchangeably. Porosity is the ratio of void volume to solid volume (or solid mass) of a porous material, and the units for porosity typically are % porosity or  $\text{cm}^3/\text{g}$ . Yet Ivaldi characterizes porosity using units of "microns" and "fractions of a micron." This, of course, is meaningless. "Microns" and "fractions of a micron" are *not* units used to characterize porosity; nor are they units used to characterize gas permeability. For this reason alone, the Ivaldi patent is indefinite and fails to teach persons skilled in the art the use of a porous frame having a prescribed gas permeability to oxygen or nitrogen.

A porous structure can be characterized by specifying many different physical parameters, including its porosity, pore size, pore shape (i.e., circularity of cross-sectional shape), pore tortuosity (i.e., nonlinearity of pore path), and pore surface area. *All* of these identified parameters affect the porous structure's gas permeability. Structures having the same porosity and pore size, but different pore shapes, different degrees of pore tortuosity, or different degrees of pore surface area, will have *different* gas permeability values.

However, parameters such as pore shape and pore tortuosity are difficult to characterize. For that reason, the preferred approach for characterizing a porous structure is to characterize its gas permeability directly. Gas permeability inherently incorporates *all* of these parameters, i.e., porosity, pore size, pore shape, pore tortuosity, and pore surface area.

Despite the deficiencies of characterizing a structure's gas permeability using merely the parameters of porosity and pore size, that is all that Ivaldi specifies. Specifying only porosity or pore size (and doing so, in the case of porosity, using improper units of "microns" or "fractions of a micron") certainly constitutes a *non*-enabling disclosure of the feature of

Applicants' claimed invention calling for the porous frame to have a predetermined gas permeability.

Applicants further disagree with the Examiner's assertion, quoted above, that Ivaldi teaches a porous frame "made from sintered metal particles having pores sized from sub-micron to plural microns each." Ivaldi's sintered metal particles are *not* disclosed as having any pores at all. What the patent, in fact, discloses is that the "metal powder particles or filaments [are] bonded at their contact points by sintering, which may create a continuous, well-defined network of pores *between* the particles or filaments." It is the porosity provided by *these* pores, not by pores in the metal particles themselves, that the patent states "may be specified in microns, or in fractions of a micron." Regardless, as discussed above, the patent's discussion of this porosity is meaningless, because porosity is not measured in microns or fractions of a micron.

Moreover, as the Examiner has acknowledged, the Ivaldi patent fails to disclose many features set forth in claims 1-24. Specifically, with respect to independent claim 1, the Ivaldi patent fails to disclose a porous frame having "a gas permeability to oxygen or nitrogen higher than about 10 ml.mm/cm<sup>2</sup>.min.MPa" and "a coefficient of thermal expansion between 0.01 ppm/°C and 10ppm/°C." To make up for this failure of the Ivaldi patent, the Examiner asserted that these features are disclosed by the secondary Okada publication. Applicants respectfully disagree.

The Okada publication discloses a pellicle frame 3 formed of quartz glass, which is said to have "higher rigidity as compared with conventional aluminum." (See, Paragraph [0022].) This quartz glass material has a coefficient of thermal expansion substantially matching that of an overlaying pellicle sheet 4. The Examiner's assertion that "Okada et al. teach a pellicle having a frame made of *porous* quartz glass (abstract, paragraph [0014])" is *incorrect*. Okada's vent holes 1, which have sizes on the order of a millimeter or more (see Table 1 of the publication), are orders of magnitude larger than the claimed pores having an average size in the range of "0.001 micrometers to 10 micrometers." Moreover, Okada's quartz glass pellicle frame is *not* specified to have any particular porosity or any particular gas permeability.



Moreover, the Okada publication even teaches that micro-cracks in the pellicle frame should be *eliminated*:

Further, with a view to *eliminating micro-cracks of the pellicle frame*, it is preferred to immerse the pellicle frame in an etching tank to subject the entire pellicle frame to etching.” (Italics added.)

Okada publication, paragraph [0035].

It, therefore, will be appreciated that the pellicle frames of the Ivaldi patent and the Okada publication use entirely different approaches to achieve pressure equalization and purging: Ivaldi uses a porous metallic frame (of indefinite pore structure and unspecified gas permeability), and Okada uses a non-porous quartz glass frame having special vent holes formed on its opposing side walls.

At best, if persons skilled in the art had been motivated to improve on Ivaldi's pellicle frame to avoid drawbacks caused by CTE variations, they would have *substituted* Okada's quartz pellicle frame. There is no teaching or suggestion that such persons would have fashioned an entirely new pellicle frame incorporating the porosity of Ivaldi's metallic frame and the coefficient of thermal expansion of Okada's frame. Moreover, even if they did so, neither reference teaches the importance of providing a gas permeability to oxygen or nitrogen higher than the specified threshold of about 10 ml.mm/cm<sup>2</sup>.min.MPa.

The Examiner's § 103(a) rejection relies on improper hindsight, picking and choosing selected features from different references to arrive at Applicants' claimed invention. This is improper. For this reason, the rejection of claims 1-24 is improper and should be withdrawn.

#### New Claims 56 and 57

By this Amendment, Applicants have added new claims 56 and 57 to the application. Both new claims depend from independent claim 1, with claim 56 defining the porous frame to be “free of any vent holes having a cross-dimension of 50 micrometers or more,” and with claim 57 defining the porous frame to be “free of any vent holes sized to allow


the diffusion of particles larger than 10 micrometers.” Support for these two new claims is found throughout the original specification, including the drawings and paragraphs [0012]–[0014] and [0017]. These claims further distinguish over the disclosures of the Ivaldi patent and the Okada publication, and they are properly allowable.

### **Conclusion**

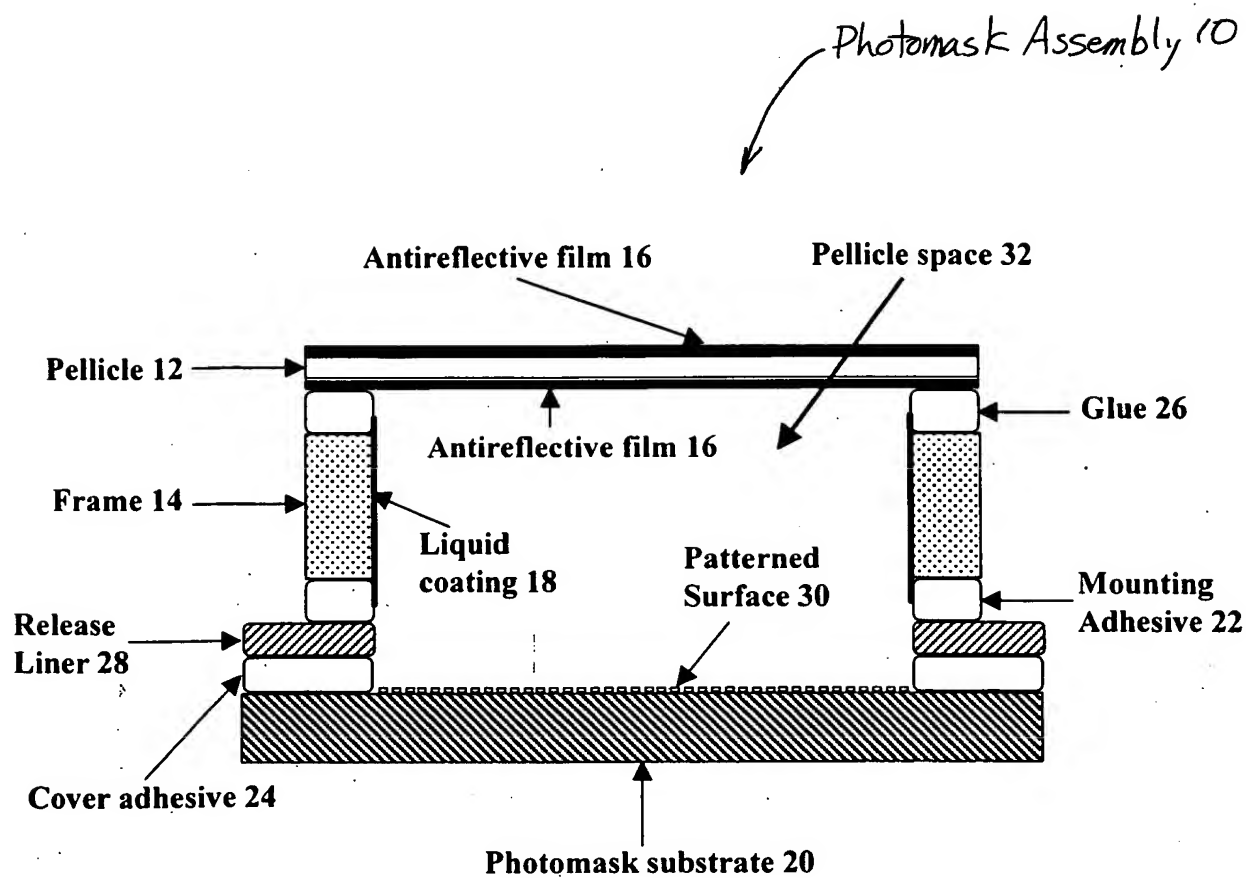
This application should now be in condition for a favorable action. Allowance of claims 1-24 and 56-57 is respectfully requested. If the Examiner believes that a telephone conference with Applicants’ undersigned representative might expedite prosecution of the application, he is respectfully requested to call at the telephone number indicated below.

Date: September 15, 2005

Respectfully submitted,  
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**FIG. 1**

*Prior Art*

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# **POLYMER HANDBOOK**

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**FOURTH EDITION**

**Editors**

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**Associate Editors**

**A. ABE  
D. R. BLOCH**



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# Permeability and Diffusion Data

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## A. INTRODUCTION

The transmission of molecules through polymer films is named "permeability". There are many dimensions and units found in the literature for the general expression "permeability". In this paper the permeability coefficient is used. It has the dimension

$$P = \frac{(\text{quantity of permeant}) \times (\text{film thickness})}{(\text{area}) \times (\text{time}) \times (\text{pressure drop across the film})}$$

and is the best definition for permeability.

The permeability coefficient, in a strict sense, is not only a function of the chemical structure of the polymer. It also varies with the morphology of the polymer and depends on many physical factors such as density, crystallinity, and orientation. However, the chemical structure of a polymer can be considered to be the predominant factor which controls the magnitude of the permeability coefficient.

The following general trends in permeability, as related to some influencing factors, may be useful for the proper interpretation of the tables:

*Density* can be regarded as a measure of the free volume between the molecules of the polymer structure. In general, the higher the density, the lower is the permeability.

*Crystallinity* of a semicrystalline polymer reduces the permeability significantly compared to the value of the corresponding amorphous polymer; i.e., the higher the degree of crystallinity, the lower the permeability. The crystallinity and the density of a polymer are strongly related. The higher the crystallinity the higher is the density of a given polymer.

*Molecular mass* of a polymer has been found to have little effect on the permeability of polymers, except at a very low range of molecular masses.

*Orientation* of polymer molecules reduces the permeability.

*Crosslinking* decreases the permeability, especially for higher degrees of crosslinking and for large molecular size permeants.

*The method and degree of vulcanization* has a significant effect on the permeability of elastomers.

*Plasticizers* increase the permeability.

*Humidity* increases the permeability of some hydrophilic polymers.

*Liquid* permeants have the same permeabilities as their corresponding saturated vapors, though higher permeabilities may occur especially if parts of the polymer are being dissolved.

*Solution-cast films* have variable permeabilities depending upon the kind of solvent used and the drying technique. Poor solvents tend to yield films of higher permeability.

*Fillers*, usually inorganic fillers, decrease the permeability; however, the effect is complicated by the type, shape, and amount of filler and its interaction with the polymer.

*Thickness of film* does not, in principle, affect the permeability coefficient, the diffusion coefficient, and the solubility coefficient. In practice, different values may be obtained from films of variable thickness, which in turn may be due to differences in drawing, orientation, and crystallinity.

If a permeant does not interact with the polymer under investigation, the permeability coefficient is characteristic for the permeant-polymer system. This is the case with the permeation of many gases, such as  $H_2$ , He,  $N_2$ ,  $O_2$ , and  $CO_2$ , through many polymers. On the other hand, if a permeant interacts with the polymer, the permeation coefficient is no longer a constant, and may depend on the special conditions of the measurement and the history of the polymer film. In such cases, a single value of the permeability coefficient does not represent the characteristic permeability of the polymer, and it is necessary to know the dependency of the permeability coefficient on all possible variables in order to obtain the complete profile of the permeability of the polymer.

In these cases, the transmission rate, which has the dimension

$$Q = \frac{(\text{quantity of permeant})}{(\text{area}) \times (\text{time})}$$

is often used for practical purposes. Since the transmission rate,  $Q$ , includes neither the pressure of the permeant nor the thickness of the polymer in its dimension, it is necessary to know either the pressure or the concentration of the permeant and the thickness of the polymer under the conditions of measurement.

For both  $P$  and  $Q$ , the quantity of permeant can be expressed by mass, moles, or gaseous volume at standard temperature and pressure. These can readily be converted from one unit into another.

The preferred SI unit of the permeability coefficient used in this book is

$$\text{unit of } P : \frac{\text{cm}^3(273.15 \text{ K}; 1.013 \times 10^5 \text{ Pa}) \times \text{cm}}{\text{cm}^2 \times \text{s} \times \text{Pa}}$$

where  $(273.15 \text{ K}; 1.013 \times 10^5 \text{ Pa})$  means standard temperature and pressure (STP). Therefore permeability coefficients given in this paper are in the range of  $10^{-11}$  –  $10^{-16} \text{ cm}^3 \times \text{cm}/\text{cm}^2 \times \text{s} \times \text{Pa}$  for many polymers and permeants.

The mostly used units and their conversion factors are listed in Table B.

The permeation of molecules through flawless polymers occurs by the steps of dissolution of a permeant in the polymer and diffusion of the dissolved permeant. The product of the diffusion coefficient  $D$  and the solubility coefficient  $S$  is referred to as the permeability coefficient.

$$P = D \times S$$

Units of  $D$  and  $S$  used in these tables are

$$\text{unit of } D : \frac{\text{cm}^2}{\text{s}}$$

$$\text{unit of } S : \frac{\text{cm}^3(273.15 \text{ K}; 1.013 \times 10^5 \text{ Pa})}{\text{cm}^3 \times \text{Pa}}$$

The solubility coefficients cited in the following tables are often calculated by

$$S = \frac{P}{D}$$

The temperature dependence of the permeability coefficient  $P$ , the diffusion coefficient  $D$ , and the solubility coefficient  $S$  can be represented by

$$P = P_0 \times \exp(-E_P/RT)$$

$$D = D_0 \times \exp(-E_D/RT)$$

and

$$S = S_0 \times \exp(-E_S/RT)$$

Consequently

$$E_P = E_D + E_S$$

where  $E_P$  is the activation energy of permeation,  $E_D$  the activation energy of diffusion, and  $E_S$  the heat of solution.  $P_0$ ,  $D_0$ , and  $S_0$  are the pre-exponential factors. Values of  $E_P$ ,  $E_D$ , and  $E_S$  are given in kJ/mol in the following tables.  $R$  is the gas constant ( $8.3144 \times 10^{-3}$  kJ/K mol);  $T$  is the temperature in K. In the following tables the temperature range is given in which  $P_0$ ,  $E_P$ ,  $E_D$ , and  $E_S$  are relevant, as

far as the authors have reported it. The permeability coefficient can be determined for a given temperature by means of the pre-exponential factor  $P_0$  and the activation energy of permeation  $E_P$ . In the following tables, permeability, diffusion, and solubility coefficients are listed for many polymers. The pre-exponential factor  $P_0$ , the activation energy of permeation  $E_P$ , the activation energy of diffusion  $E_D$ , and the heat of solution  $E_S$  are also given. The pre-exponential factors  $D_0$  and  $S_0$  can be determined by the following equations:

$$D_0 = D \times \exp(E_D/RT)$$

$$S_0 = S \times \exp(E_S/RT)$$

## B. CONVERSION FACTORS FOR VARIOUS UNITS OF THE PERMEABILITY COEFFICIENT

Multiplication factors to obtain $P$ in:			
From	$\frac{[\text{cm}^3][\text{cm}]}{[\text{cm}^2][\text{s}][\text{cm Hg}]}$	$\frac{[\text{cm}^3][\text{cm}]}{[\text{cm}^2][\text{s}][\text{Pa}]}$	$\frac{[\text{cm}^3][\text{cm}]}{[\text{m}^2][\text{day}][\text{atm}]}$
$\frac{[\text{cm}^3][\text{cm}]}{[\text{cm}^2][\text{s}][\text{cm Hg}]}$	1	$7.5 \times 10^{-4}$	$6.57 \times 10^{10}$
$\frac{[\text{cm}^3][\text{mm}]}{[\text{cm}^2][\text{s}][\text{cm Hg}]}$	$10^{-1}$	$7.5 \times 10^{-5}$	$6.57 \times 10^9$
$\frac{[\text{cm}^3][\text{cm}]}{[\text{cm}^2][\text{s}][\text{atm}]}$	$1.32 \times 10^{-2}$	$9.87 \times 10^{-6}$	$8.64 \times 10^8$
$\frac{[\text{cm}^3][\text{mil}]}{[\text{cm}^2][\text{day}][\text{atm}]}$	$3.87 \times 10^{-14}$	$2.90 \times 10^{-17}$	$2.54 \times 10^{-3}$
$\frac{[\text{in}^3][\text{mil}]}{[100\text{in}^2][\text{day}][\text{atm}]}$	$9.82 \times 10^{-12}$	$7.37 \times 10^{-15}$	$6.45 \times 10^{-1}$
$\frac{[\text{cm}^3][\text{cm}]}{[\text{m}^2][\text{day}][\text{atm}]}$	$1.52 \times 10^{-11}$	$1.14 \times 10^{-14}$	1
$\frac{[\text{cm}^3][\text{cm}]}{[\text{m}^2][\text{day}][\text{bar}]}$	$1.54 \times 10^{-11}$	$1.16 \times 10^{-14}$	1.01
$\frac{[\text{cm}^3][\text{cm}]}{[\text{cm}^2][\text{s}][\text{Pa}]}$	$1.33 \times 10^3$	1	$8.75 \times 10^{13}$

## C. TABLES

TABLE 1. PERMEABILITY COEFFICIENTS, DIFFUSION COEFFICIENTS, AND SOLUBILITY COEFFICIENTS OF POLYMERS

Units used in the tables are as follows:  $P$ ,  $P_0$  in  $\text{cm}^3$  (273.15 K;  $1.013 \times 10^5$  Pa)  $\times$   $\text{cm}/(\text{cm}^2 \times \text{s} \times \text{Pa})$ ;  $D$  in  $\text{cm}^2/\text{s}$ ;  $S$  in  $\text{cm}^3$  (273.15 K;  $1.013 \times 10^5$  Pa)  $/(\text{cm}^3 \times \text{Pa})$ ;  $E_P$ ,  $E_D$ ,  $E_S$  in kJ/mol;  $T$  in  $^\circ\text{C}$ ; (273.15 K;  $1.013 \times 10^5$  Pa) means standard temperature and pressure (STP).

Polymer	Permeant	$T$	$P (\times 10^{13})$	$D (\times 10^6)$	$S (\times 10^6)$	Temp. range	$P_0 (\times 10^7)$	$E_P$	$E_D$	$E_S$	Refs.
1.1. POLY(ALKANES)											
Poly(ethylene) LLDPE	$\text{C}_2\text{H}_4\text{O}$	30	68.9	0.031	225						80
Poly(ethylene) density 0.914 g/cm <sup>3</sup> , LDPE	$\text{H}_2$	25	7.4	0.474	1.58						49
	$\text{D}_2$	25	6.6	0.476	1.38						49
	He	25	3.7	6.8	0.0544	5-60	4.62	34.8	24.7	10.1	16
	$\text{O}_2$	25	2.2	0.46	0.472	5-60	66.5	42.7	40.2	2.5	16
	Ar	25	2.1	0.36	0.571	5-60	174	45.2	42.3	2.9	16
	Ne	25	0.48	2.42	0.020						49
	Kr	25	2.15	0.169	1.28						49
	Xe	25	4.01	0.069	5.82						49
	$\text{CO}_2$	25	9.5	0.372	2.54	5-60	62.0	38.9	38.5	0.4	16



## Review

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# Membrane-based gas separation

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### Abstract

An exhaustive treatment of the past decade of intense activity in the membrane-based gas separation field would require an entire book and provide more detail than necessary to capture the essence of this dynamic field. This review seeks to define the current *scientific, technological* and *commercial* boundaries of the field of membrane-based gas separation and to project the position of these boundaries for the immediate future. The most understandable connection between these three areas lies in the material science and engineering achievements and limitations that dominate the application of the technology at the present time. Achievements over the past ten to fifteen have promoted the current strong interest in membrane-based gas separations, and the promise of steady progress toward removing remaining limitations suggests the likelihood of its long term growth as a field. Material selection, membrane formation, and trends in module and system characteristics are discussed in the context of the challenges and opportunities that exist for major commercial applications of the technology.

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stream face of a membrane. The driving force for the process is a chemical potential difference related to the concentration difference imposed by the partial pressure of the permeation species at the upstream and downstream membrane faces. While these concepts capture the essence of the process, they don't allow the separate consideration of the contributions of the processes of solution and diffusion, so it is useful to refine these notions with a quantitative expression.

Fortunately, a framework for discussion of the material science aspects of gas separation membranes requires only a few simple relations and can be traced back to the early work of Von Wroblewski [87]. The "permeability",  $P_A$ , of a membrane of a given gas (A) in a membrane material is a parameter equal to the pressure-and-thickness-normalized flux. This parameter provides the overall measure of the ease of transporting the gas through the material.

$$P_A = (\text{flux of A}) [l] / [\Delta p_A] \quad (2)$$

Since the permeability is independent of the thickness of the membrane, it is a fundamental property of the polymeric material, but it does not consider the detailed solution-diffusion nature of the process described by Graham. To achieve this description, the permeability can be written as a product of a thermodynamic factor,  $S_A$ , called the solubility coefficient, and a kinetic parameter,  $D_A$ , called the diffusion coefficient.

$$P_A = [S_A][D_A] \quad (3)$$

The coefficients in eqn. (3) can themselves be complex functions of many variables. These complicating factors may include the type and amount of additional sorbed penetrants in the neighborhood of the permeating penetrant as well as the temperature which causes the agitation of the polymer segments [15,16,88]. Recently, it has been shown that even prior thermal or penetrant exposure history of the matrix

in the case of glassy polymers can have major effects on the solubility and diffusivity coefficients long after the perturbing influence is removed. All of these complicating factors will be touched on briefly in subsequent sections. As a practical matter, however, the intrinsic physical and chemical natures of the polymer comprising the matrix are the major determinants of these coefficients and will be considered prior to considering these complications.

If the upstream and downstream partial pressures of all components are known, the upstream and downstream solubilities of component A ( $C_{A2}$  and  $C_{A1}$ , resp.) are determined. Subscripts "2" and "1" refer to the upstream and downstream faces of the membrane respectively. Although additional components in a mixture may influence the transport of component A, for simplicity, only cases will be considered in this section where such components are held essentially constant in the measurements of the pertinent sorption and transport parameters. In this case, the sorption and transport coefficients are, at most, functions of the concentration of the component under consideration, and many cases may vary weakly enough to be considered constant. Under these constraints, the apparent diffusion and solubility coefficients of component A can be expressed as average parameters characterizing the overall environment sampled by the penetrant as it moves from the upstream to the downstream face of the membrane, viz.,

$$D_A = \int_{C_{A1}}^{C_{A2}} D(C) dC / \int_{C_{A1}}^{C_{A2}} dC \quad (4a)$$

$$S_A = (C_{A2} - C_{A1}) / (p_{A2} - p_{A1}) \quad (4b)$$

The separation factor for component A vs. B,  $\alpha_{AB}$ , is defined in terms of the downstream and upstream mole fractions ( $X$ ) of components A and B, respectively, viz.,

$$\alpha_{AB} = (X_{A1}/X_{B1}) / (X_{A2}/X_{B2}) \quad (5)$$

hatched, undesirable area, below the solid line is associated with "low free volume glasses" and "rubbery polymers". The poor mobility selectivity and high diffusivities in rubbery media noted earlier produce high permeabilities and low overall permselectivities. On the other hand, the well-packed, low free volume glasses, give equally unattractively low permeabilities and high selectivities. The solid line represents "optimistic" tradeoff behavior typical of commercially available engineering resins, such as standard bisphenol-A polycarbonate which is represented by "PC" on this line. Commercial polysulfone lies close to PC on this plot with an  $O_2$  permeability of 1.1 barrers and an  $O_2/N_2$  ideal selectivity of 6.0 at 35°C [15]. Given current fabrication abilities to make thin selective layers of approximately 1000 Å, commercially attractive flux rates require permeabilities of at least 1 barrer<sup>a</sup>. In some cases, such as low concentration  $O_2$  enrichment [73] or aircraft inert gas generation, much higher fluxes may be needed to achieve economical performance.

The desirable regime to the upper right in Fig. 14 corresponds to high free volume, low segmental mobility glasses. A "model polycarbonate" structure can be represented in Fig. 15 with various "Y's" and "X's" corresponding to the structure shown in Table 5, e.g. standard polycarbonate corresponds to an isopropylidene as Y and H's at the X positions. Tetramethyl substituted polycarbonate, TMPC, has methyl groups at all four X positions and no change in the isopropylidene Y. This combination gives both inhibited motion around the carbonate linkage, and inhibited packing due to restriction of facile "nesting" conformations of the phenyl rings. Consistent with the earlier mentioned rule for structural optimization, this combined increase in FFV and rigidity the matrix, results in a three-fold increase in produc-

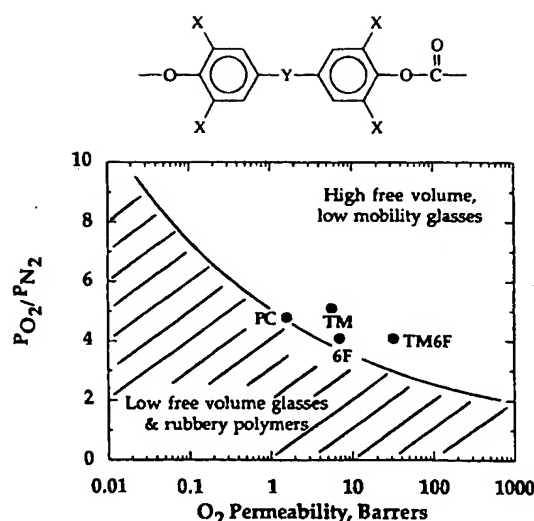


Fig. 15. "Tradeoff" curve for  $O_2/N_2$  with the points added for the systematically varied group of polycarbonates in Table 5 illustrating the ability to deviate favorably from the standard tradeoff curve behavior. Note the abscissa is a log scale, so the deviation is significant.

tivity without a loss in permselectivity compared to standard PC (Table 6).

The less desirable effects of simply inhibiting packing with little change in sub- $T_g$  segmental mobility is illustrated by 6FPC, corresponding to leaving the X's as compact hydrogens, but with  $-C(CF_3)_2-$  group at the Y position. The bulky  $-C(CF_3)_2-$  groups in the isopropylidene position lock the phenyl rings into packing inhibiting orientations. Nevertheless, they do essentially nothing to hinder rocking motions around the mobile carbonate link, as indicated by the unchanged sub- $T_g$  transition temperature in Table 5 [99,15]. The 6FPC has a higher FFV and permeability than TMPC (which has space-filling methyl substituents), but a lower selectivity since rotation mobility around its mobile carbonate link is not affected. The use of the FFV rather than simple free volume as an intersegmental packing measure avoids biasing results when heavy elements such as fluorine are present [110,111]. With both substitutions on the same unit, i.e.

<sup>a</sup>1 Barrer =  $10^{-10} \frac{\text{cm}^3(\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}} = 2.98 \frac{\text{mmol}}{\text{m} \cdot \text{sec} \cdot \text{TPa}}$



Designation: D 1434 – 82 (Reapproved 2003)

## Standard Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting<sup>1</sup>

This standard is issued under the fixed designation D 1434; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method covers the estimation of the steady-state rate of transmission of a gas through plastics in the form of film, sheeting, laminates, and plastic-coated papers or fabrics. This test method provides for the determination of (1) gas transmission rate (GTR), (2) permeance, and, in the case of homogeneous materials, (3) permeability.

1.2 Two procedures are provided:

1.2.1 *Procedure M*—Manometric.

1.2.2 *Procedure V*—Volumetric.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Referenced Documents

2.1 *ASTM Standards*:<sup>2</sup>

D 618 Practice for Conditioning Plastics for Testing

D 1898 Practice for Sampling of Plastics

### 3. Terminology

3.1 *Definitions of Terms Specific to This Standard*:

3.1.1 *gas transmission rate, GTR*—the quantity of a given gas passing through a unit of the parallel surfaces of a plastic film in unit time under the conditions of test. The SI unit of GTR is  $1 \text{ mol}/(\text{m}^2 \cdot \text{s})$ . The test conditions, including temperature and partial pressure of the gas on both sides of the film, must be stated. Other factors, such as relative humidity and hydrostatic pressure, that influence the transport of the gas must also be stated. The inch-pound unit of GTR, a commonly

used unit of GTR, is  $1 \text{ mL (STP)}/(\text{m}^2 \cdot \text{d})$  at a pressure differential of one atmosphere.

3.1.2 *permeance, P*—the ratio of the gas transmission rate to the difference in partial pressure of the gas on the two sides of the film. The SI unit of permeance is  $1 \text{ mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ . The test conditions (see 5.1) must be stated.

3.1.3 *permeability, P*—the product of the permeance and the thickness of a film. The permeability is meaningful only for homogeneous materials, in which it is a property characteristic of the bulk material. This quantity should not be used unless the constancy of the permeability has been verified using several different thicknesses of the material. The SI unit of  $P$  is  $1 \text{ mol}/(\text{m} \cdot \text{s} \cdot \text{Pa})$ . The test conditions (see 3.1) must be stated.

NOTE 1—One millilitre (STP) is  $44.62 \mu\text{mol}$ , one atmosphere is  $0.1013 \text{ MPa}$ , and one day is  $86.4 \times 10^3 \text{ s}$ . GTR in SI units is obtained by multiplying the value in inch-pound units by  $5.160 \times 10^{-10}$ . Additional units and conversions are shown in Appendix X1.

3.1.4 *steady state*—the state attained when the amount of gas absorbed in the film is in equilibrium with the flux of gas through the film. For Method V this is obtained when the GTR is constant.

### 4. Summary of Test Method

4.1 The sample is mounted in a gas transmission cell so as to form a sealed semibarrier between two chambers. One chamber contains the test gas at a specific high pressure, and the other chamber, at a lower pressure, receives the permeating gas. Either of the following procedures is used:

4.1.1 *Procedure M*—In Procedure M the lower pressure chamber is initially evacuated and the transmission of the gas through the test specimen is indicated by an increase in pressure.

4.1.2 *Procedure V*—In Procedure V the lower pressure chamber is maintained near atmospheric pressure and the transmission of the gas through the test specimen is indicated by a change in volume.

### 5. Significance and Use

5.1 These measurements give semiquantitative estimates for the gas transmission of single pure gases through film and sheeting. Correlation of measured values with any given use, such as packaged contents protection, must be determined by

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee F02 on Flexible Barrier Materials and is the direct responsibility of Subcommittee F02.30 on Test Methods.

Current edition approved July 30, 1982. Published November 1982. Originally published as D 1434 – 56 T. Last previous edition D 1434 – 75.

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

experience. The gas transmission rate is affected by conditions not specifically provided for in these tests, such as moisture content (Note 2), plasticizer content, and nonhomogeneities. These tests do not include any provision for testing seals that may be involved in packaging applications.

NOTE 2—The tests are run using gas with 0 % moisture changes.

5.2 Interlaboratory testing has revealed that permeances measured by these procedures exhibit a strong dependence on the procedure being used, as well as on the laboratory performing the testing. Agreement with other methods is sometimes poor and may be material-dependent. The materials being tested often affect the between-laboratory precision. The causes of these variations are not known at this time. It is suggested that this method not be used for referee purposes unless purchaser and seller can both establish that they are measuring the same quantity to a mutually agreed upon level of precision.

5.3 Use of the permeability coefficient (involving conversion of the gas transmission rate to a unit thickness basis) is not recommended unless the thickness-to-transmission rate relationship is known from previous studies. Even in essentially homogeneous structures, variations in morphology (as indicated, for example, by density) and thermal history may influence permeability.

## 6. Test Specimen

6.1 The test specimen shall be representative of the material, free of wrinkles, creases, pinholes, and other imperfections, and shall be of uniform thickness. The test specimen shall be cut to an appropriate size (generally circular) to fit the test cell.

6.2 The thickness of the specimen shall be measured to the nearest 2.5  $\mu\text{m}$  (0.1 mil) with a calibrated dial gage (or equivalent) at a minimum of five points distributed over the entire test area. Maximum, minimum, and average values should be recorded. An alternative measure of thickness involving the weighing of a known area of specimens having a known density is also suitable for homogeneous materials.

## 7. Conditioning

7.1 *Standard Conditioning*—Condition all test specimens at  $23 \pm 2^\circ\text{C}$  ( $73.4 \pm 3.6^\circ\text{F}$ ) in a desiccator over calcium chloride or other suitable desiccant for not less than 48 h prior to test in accordance with Practice D 618, for those tests where conditioning is required. In cases of disagreement, the tolerances shall be  $\pm 1^\circ\text{C}$  ( $\pm 1.8^\circ\text{F}$ ).

7.2 *Alternative Conditioning*—Alternatives to 7.1 may be used for conditioning the specimens provided that these conditions are described in the report.

## 8. Sampling

8.1 The techniques used in sampling a batch of material to be tested by these procedures must depend upon the kind of information that is sought. Care should be taken to ensure that samples represent conditions across the width and along the length of rolls of film. Practice D 1898 provides guidelines for deciding what procedures to use in sampling a batch of

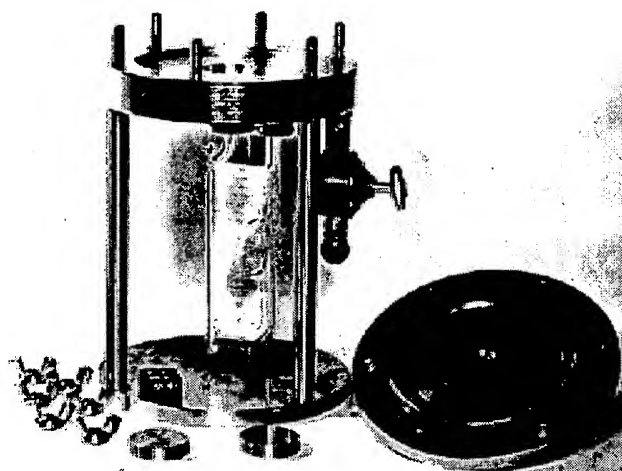


FIG. 1 Manometric Gas Transmission Cell

material. Enough specimens must be tested to ensure that the information obtained is representative of the batch or other lot size being tested.

## PROCEDURE M

(Pressure changes in the manometric cell may be determined by either visual or automatic recording.)

### MANOMETRIC VISUAL DETERMINATION

#### 9. Apparatus

9.1 The apparatus shown in Fig. 1 and Fig. 2 consists of the following items:<sup>3</sup>

9.1.1 *Cell Manometer System*—The calibrated cell manometer leg, which indicates the pressure of transmitted gas, shall consist of precision-bore glass capillary tubing at least 65 mm long with an inside diameter of 1.5 mm.

9.1.2 *Cell Reservoir System*, consisting of a glass reservoir of sufficient size to contain all the mercury required in the cell.

9.1.3 *Adapters*—Solid and hollow adapters for measurement of widely varying gas transmission rates. The solid adapter provides a minimum void volume for slow transmission rates. The hollow adapter increases the void volume by about a factor of eight for faster transmission rates.

9.1.4 *Cell Vacuum Valve*, capable of maintaining a vacuum-tight seal.<sup>4</sup>

9.1.5 *Plate Surfaces*, that contact the specimen and filter paper shall be smooth and flat.

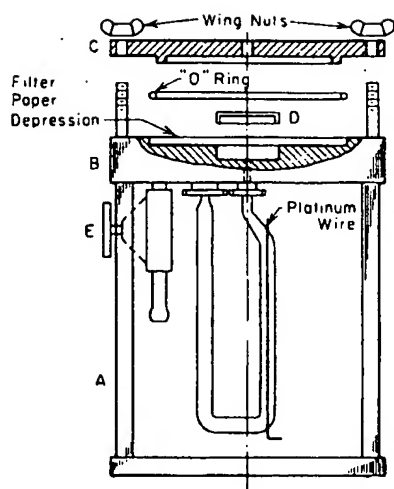
9.1.6 *O-Ring*, for sealing the upper and lower plates.

9.1.7 *Pressure Gage*, mechanical or electrical type with a range from 0 to 333 kPa absolute. Used for measuring upstream gas pressure.

9.1.8 *Barometer*, suitable for measuring the pressure of the atmosphere to the nearest 133 Pa.

<sup>3</sup> The Dow gas transmission cell supplied by Custom Scientific Instruments, Inc., Whippany, NJ, has been found satisfactory for this purpose.

<sup>4</sup> The Demi-G Valve (1/4-in. IPS) manufactured by G. W. Dahl Co., Inc., Bristol, RI, or a precision-ground glass stopcock, meets this requirement.



A—Supporting Legs  
B—Lower Plate  
C—Upper Plate  
D—Adapter  
E—Vacuum Valve

FIG. 2 Schematic View of Gas Transmission Cell

9.1.9 *Vacuum Gage*, to register the pressure during evacuation of the system to the nearest 13 Pa.

9.1.10 *Vacuum Pump*, capable of reducing the pressure in the system to 26 Pa or less.

9.1.11 *Needle Valve*, for slowly admitting and adjusting the pressure of the test gas.

9.1.12 *Cathetometer*, to measure the height of mercury in the cell manometer leg accurately. This instrument should be capable of measuring changes to the nearest 0.5 mm.

9.1.13 *Micrometer*, to measure specimen thickness, graduated to 2.5  $\mu\text{m}$  (0.1 mil) or better.

9.1.14 *Elevated-Temperature Fittings*—Special cell fittings are required for high-temperature testing.

## 10. Materials

10.1 *Test Gas*—The test gas shall be dry and pure. The ratio of the volume of gas available for transmission to the volume of gas transmitted at the completion of the test shall be at least 100:1.

10.2 *Mercury*—Mercury used in the cell shall be triple distilled, checked regularly for purity, and replaced with clean mercury when necessary.

10.2.1 **Warning**—Very low concentrations of mercury vapor in the air are known to be hazardous. Guidelines for using mercury in the laboratory have been published by Steere.<sup>5</sup> Be sure to collect all spilled mercury in a closed container. Transfers of mercury should be made over a large plastic tray. Under normal daily laboratory-use conditions, the cells should be cleaned about every 3 months. Dirty mercury is indicated when the drop of the capillary becomes erratic or when mercury clings to the side of the capillary, or both. Whenever

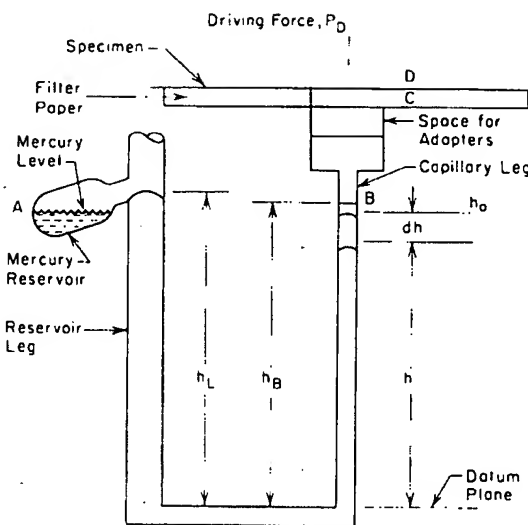


FIG. 3 Cell Manometer with Test Specimen in Place

such discontinuities occur, the mercury should be removed and the cell cleaned as follows:

- (1) Wash with toluene (to remove greases and oils).
- (2) Wash with acetone (to remove toluene).
- (3) Wash with distilled water (to remove acetone).
- (4) Wash with a 1 + 1 mixture of nitric acid and distilled water (to remove any mercury salts that may be present). This operation may be repeated if necessary in order to ensure complete cleaning of glassware.
- (5) Wash with distilled water (to remove nitric acid).
- (6) Wash with acetone (to remove water).
- (7) Dry the cell at room temperature or by blowing a small amount of clean dry air through it.

## 11. Calibration

11.1 Each cell should be calibrated at the test temperature as follows (Fig. 3):

11.1.1 Determine the void volume of the filter paper from the absolute density of its fiber content (Note 3), the weight of the filter paper, and its apparent volume (Note 4). Express the void volume determined in this way in microlitres and designate as  $V_{CD}$ .

NOTE 3—Any high-grade, medium-retention qualitative nonashing cel-lulosic filter paper, 90 mm in diameter will be satisfactory for this purpose. Cellulose fiber has an approximate density of 1.45 g/mL.

NOTE 4—The apparent volume may be calculated from the thickness and diameter of the filter paper.

11.1.2 Determine the volume of the cell manometer leg from B to C, Fig. 3, by mercury displacement. (Since the void volume of the adapters is included in this part of the calibration, the volume from B to C should be determined twice, once with the solid adapter in place, and once with the hollow.) This volume is obtained by dividing the weight of the mercury displaced by its density (Note 5). Determine this volume to nearest 1  $\mu\text{L}$  and designate as  $V_{BC}$ .

NOTE 5—The density of mercury at 23°C is 13.54 g/mL.

11.1.3 Determine the volume, in microlitres, of the cell manometer leg from A to B, Fig. 3, by mercury displacement.

<sup>5</sup> Steere, N. E. "Mercury Vapor Hazards and Control Measures" in Handbook of Laboratory Safety, N. V. Steere, Ed., CRC Press Inc., Boca Raton, FL, 1979.

Determine the average cross-sectional area of the capillary by dividing this volume by the length (expressed to the nearest 0.1 mm) from *A* to *B*. Determine this area to the nearest 0.01 mm<sup>2</sup> and designate as *a<sub>c</sub>*.

11.1.4 Determine the area of the filter paper cavity to the nearest 1 mm<sup>2</sup>. Designate this area as *A*, the area of transmission.

11.1.5 Pour the mercury from the reservoir into the manometer of the cell by carefully tipping the cell. Record the distance from the datum plane to the upper calibration line *B* in the capillary leg as *h<sub>B</sub>*. Record the distance from the datum plane to the top of the mercury meniscus in the reservoir leg as *h<sub>L</sub>*. Determine *h<sub>B</sub>* and *h<sub>L</sub>* to the nearest 0.5 mm.

11.2 NBS Standard Reference Material 1470<sup>6</sup> is a polyester film whose permeance to oxygen gas has been certified for a range of experimental conditions. The calibration steps in 11.1 can be verified by comparing measurements obtained using this method of test in the user's laboratory with the values provided on the certificate accompanying the SRM.

## 12. Procedure

12.1 Transfer all the mercury into the reservoir of the cell manometer system by carefully tipping the cell in such a way that the mercury pours into the reservoir.

12.2 Insert the appropriate adapter in the cell body.

12.3 Center a filter paper in the lower plate cavity.

12.4 Apply a light coating of vacuum grease on the flat metal that the surface of the specimen will contact. Avoid excessive grease.

12.5 Place the conditioned specimen smoothly on the lower lightly greased plate so that it covers the filter paper and the entire exposed face of the lower plate.

12.6 Locate the O-ring on the upper plate; then carefully position this plate over the specimen and fix the plate with uniform pressure to ensure a vacuum-tight seal.

12.7 Connect the line in which the test gas will be subsequently admitted to the upper plate. (The entire cell is now directly connected to the test gas line.)

12.8 Connect the vacuum source to the nipple attached to the cell vacuum valve. Evacuate the bottom of the cell; then, with the bottom still being evacuated, evacuate the top of the cell. Close off the vacuum line to the top of the cell; then close the line to the bottom (Fig. 4).

12.9 Flush the connecting line and the top of the chamber with test gas.

12.10 Reevacuate the system in the same manner as 12.8. The cell manometer system should be evacuated to a pressure of 26 Pa or less, as indicated on the vacuum gage.

12.11 Pour mercury from the reservoir into the manometer system of the cell by carefully tipping the cell. The height of the mercury in the capillary leg should be at approximately the same level as line *B* (Fig. 3) and stationary.

NOTE 6—A leak is indicated if the height of the mercury does not remain stationary. If such a leak occurs, discontinue the test and repeat the

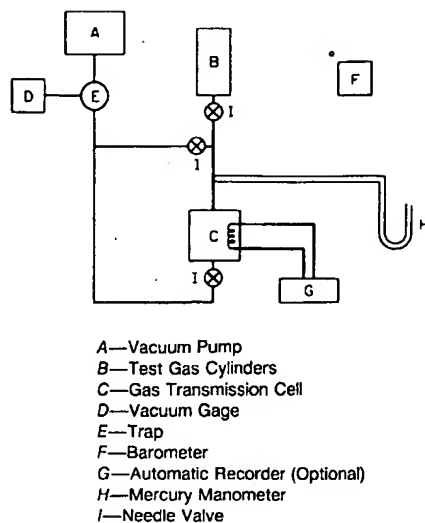


FIG. 4 Component Arrangement of Gas Transmission Equipment

entire procedure. (If a leak occurs on a second trial, this may indicate a mechanical failure of the equipment.)

12.12 Record the height of the mercury in the capillary leg, *h<sub>o</sub>*, at the start of each test, that is, immediately before the test gas has been admitted to the top of the cell.

12.13 After a suitable estimated time for attaining steady-state conditions, record the height of the mercury in the capillary leg, *h<sub>o</sub>*, to the nearest 0.5 mm and the elapsed time, *t<sub>o</sub>*, to the nearest 1 min.

12.14 Record the height of the mercury, *h*, in the capillary leg to the nearest 0.5 mm versus time, *t*, in hours, to the nearest 1 min. Take several readings (at least six are recommended) during the test. Calculate the function *g(h)* for each *t* as defined in 13.1. Plot these values versus time, (*t* - *t<sub>o</sub>*), and construct the best straight line through these points. Use any observed values of *h* and *t* for *h<sub>o</sub>* and *t<sub>o</sub>*, respectively, if these values are within the steady-state region. A nonlinear plot of *g(h)* versus (*t* - *t<sub>o</sub>*) that does not pass through the origin could indicate an improper selection of *h<sub>o</sub>* and *t<sub>o</sub>*; a new selection should then be made by using a larger mercury depression for the initial conditions.

NOTE 7—If, after all the mercury has been displaced from the capillary, any doubt exists as to the attainment of steady state, perform a check as follows:

- (1) Return the mercury to the reservoir.
- (2) Reevacuate the bottom of the cell only, leaving the top pressurized with test gas.
- (3) Repeat 12.11, 12.13, and 12.14.

12.15 Return the mercury in the capillary leg to the reservoir by tipping the cell upon completion of the test and prior to opening the cell vacuum valve.

12.16 Remove the specimen from the cell and measure the thickness with a micrometer (Note 8). Record the average of five determinations made uniformly throughout the specimen to the nearest 2.5 μm (0.1 mil).

NOTE 8—If there is reason to believe that the specimen will expand or contract during transmission, the thickness should be measured prior to 12.5, as well as after transmission. If any change in thickness occurs, a

<sup>6</sup> This material is available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, DC 20234.

note to this effect shall be included with the results.

12.17 Test three specimens with each gas.

12.18 If the requirements of 12.14 are not met in the normal atmospheric pressure test, repeat the procedure at a higher (up to 304 kPa) or lower (not less than 50 kPa) test pressure.

### 13. Calculation

13.1 Calculate the permeance,  $P$ , in SI units from the following relationship (Note 9):

$$P = g(h)/(t - t_o) \quad (1)$$

where:

$$g(h) = -\frac{1}{ART} \left[ [V_f + a(p_u + h_B - h_L)] \cdot \ln \left\{ 1 - \frac{(h_o - h)}{P_u - (h_L - h_o)} \right\} + 2a(h_o - h) \right] \quad (2)$$

- $a_c$  = area of capillary  $\overline{AB}$ , mm<sup>2</sup>,
- $A$  = area of transmission, cm<sup>2</sup>,
- $h_o$  = height of mercury in the capillary leg at the start of the actual transmission run, after steady-state conditions have been attained, mm,
- $h$  = height of mercury in cell capillary leg at any given time, mm,
- $h_B$  = maximum height of mercury in the cell manometer leg from the datum plane to upper calibration line  $B$ , mm,
- $h_L$  = height of mercury in cell reservoir leg from datum plane to top of mercury meniscus, mm,
- $P_u$  = upstream pressure of gas to be transmitted,
- $R$  = universal gas constant  $8.3143 \times 10^3$  L·Pa/(mol·K),
- $t_o$  = time at the start of the actual transmission run,  $h$ , after steady-state conditions have been attained,
- $t$  = time, h,
- $T$  = absolute temperature, K,
- $V_{BC}$  = volume from  $B$  to  $C$ ,  $\mu$ L,
- $V_{CD}$  = void volume of depression,  $\mu$ L, and
- $V_f$  = ( $V_{BC} + V_{CD}$ ),  $\mu$ L.

NOTE 9—The derivation of this equation is given in Appendix X2. Refer to Fig. 3 for location of symbols used in this equation.

13.2 A test result is defined as a single determination of the permeance of an individual sheet of material.

## MANOMETRIC RECORDING DETERMINATION

### 14. Apparatus

14.1 The description of the apparatus is identical to that in Section 9, with the omission of 9.1.12, which does not apply in this procedure, and the addition of the following apparatus:

14.2 *Resistance-Recording Instrument*—A resistance-recording instrument suitably connected to a uniform-diameter platinum wire (Note 10) that runs the calibrated length of the cell manometer leg shall be employed to measure changes in height of the mercury in the cell manometer leg versus time. This instrument shall be capable of measuring such changes to the nearest 0.5 mm.

NOTE 10—A recommended automatic recording device (Fig. 4 shows a simplified schematic of a setup utilizing an automatic recorder) consists of

No. 44 platinum wire (with a resistance of 0.8  $\Omega$ /cm) with No. 30 tungsten leads to the glass. These are connected by means of No. 16 gage three-conductor copper wire to a suitable ten-turn potentiometer in series with a resistance recorder whose full-scale range is 10 to 15  $\Omega$ .<sup>7</sup>

### 15. Materials

15.1 Same as Section 10.

### 16. Calibration

16.1 Same as Section 11, but should also include the following:

16.2 The recording instrument with the cell, lead wires, and external resistance (Note 11) in series as used in the test shall be calibrated at test temperature initially and every time after a cell has been cleaned or repaired.

NOTE 11—The external resistance should be so chosen to permit complete traverse of the chart by the pen when a change in the height of mercury equal to the height of  $A$  to  $B$  occurs (Fig. 3).

16.3 The recording system shall be calibrated as follows:

16.3.1 Allow the cell to come to constant temperature at test temperature.

16.3.2 With the top of the cell removed and the vacuum valve open, pour the mercury into the cell manometer leg such that the mercury is approximately at the same level as line  $B$  (Fig. 3) and relatively stationary. Adjust the external resistance of the recorder so that the pen indicates a chart position of zero.

16.3.3 Vary the height of the mercury column and note the position indicated by the chart pen so that a plot of chart position as ordinate versus mercury height as abscissa is obtained. A straight line should result.

16.3.4 Determine the rate of chart paper travel to the nearest 2.54 mm (0.1 in.)/h.

16.4 See 11.2 for the use of NBS Standard Reference Material 1470 in checking the calibration of the permeance measuring apparatus.

### 17. Procedure

17.1 Same as Section 12, with the following exceptions:

17.2 Adjust the pen of the resistance recording instrument by means of the external resistance so that the pen position corresponds with the height of mercury in the capillary leg as determined in Section 16.

17.3 For best results, set the chart to run at a speed that will plot the gas transmission curve at a slope of about 45° (Note 12). Once experience is gained, the proper chart speed is easily selected.

NOTE 12—This applies only to charts that have a variable-speed drive.

### 18. Calculation

18.1 For several values of  $t$  (at least six are recommended), read  $h$  from the recorder chart and plot the function  $g(h)$  versus  $t$  as defined in 12.14.

<sup>7</sup> The Minneapolis-Honeywell Regulator Co. 60V Model 153X64W8-X-41 resistance recorder has been found satisfactory for this purpose. It is recommended that a quick-change variable speed chart drive, such as that supplied by Inco Co., Division of Barry Controls, Inc., Groton, MA, be installed in the recorder.



18.2 Calculate the permeance from the equations given in 13.1.

18.3 A test result is defined as the value of a single individual determination of permeance of a film.

19.2 *Precision Glass Capillaries* or manometers with various diameters (0.25, 0.50, and 1.0 mm are recommended). The glass capillaries should have a suitable U-bend to trap the manometer liquid and a standard-taper joint to fit into the cell.

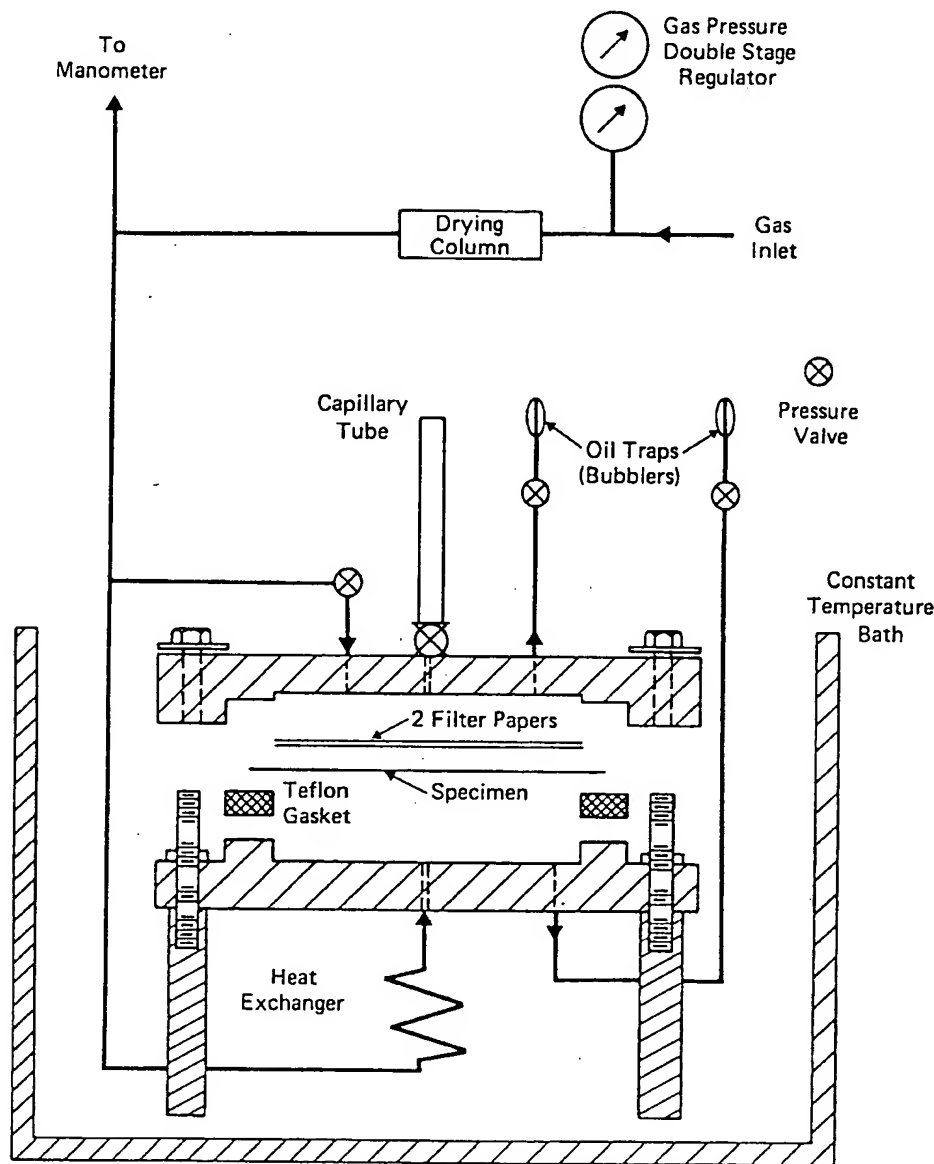


FIG. 5 Volumetric Gas Transmission Cell

## PROCEDURE V

(Volumetric determinations may be made with several similar type apparatus.)

### 19. Apparatus

19.1 *Volumetric Gas Transmission Cell*<sup>8</sup>, shown in Fig. 5.

<sup>8</sup> Suitable cells may be obtained from Custom Scientific Instruments, Whippany, NJ.

19.3 *Cathetometer* or suitable scale for measuring changes in meniscus position to the nearest 0.5 mm.

19.4 *Temperature Control*:

19.4.1 A temperature-control liquid bath is recommended for controlling the temperature of the cell body to  $\pm 0.1^\circ\text{C}$ .

19.4.2 The apparatus should be shielded to restrict the temperature variations of the capillary to  $\pm 0.1^\circ\text{C}$  during the test.

19.5 *Micrometer*, to measure specimen thickness, to the nearest  $2.5\ \mu\text{m}$  (0.0001 in.) at a minimum of five points

distributed over the entire test area. Maximum, minimum, and average values shall be recorded.

19.6 *Barometer*, suitable for measuring the pressure of the atmosphere to the nearest 133 Pa.

19.7 *Pressure Gage*, precision mechanical or electrical type for measuring absolute pressure over the range from 0 to 333 kPa.

## 20. Materials

20.1 *Cylinder of Compressed Gas*, of high purity equipped with pressure reducing valves.

20.2 *Capillary Liquid*— 4-Methyl-2-pentanone (methyl isobutyl ketone) (Note 13) or other appropriate liquid colored with a suitable dye<sup>9</sup> (Note 14).

NOTE 13—4-Methyl-2-pentanone has a vapor pressure of 933 Pa at 23°C. Erroneous results may be obtained in some cases, if the attainment of this equilibrium causes slug movement in the capillary. This may take an appreciable time, especially in small capillaries, and thereby lead to an erroneous answer. Also, the vapor of 4-methyl-2-pentanone may cause swelling of some materials, which will result in a change in the permeation rate.

NOTE 14—Mercury is not recommended for the capillary liquid except for use in calibrating cross-sectional areas because of contact angle hysteresis and resulting pressure errors (about 3 cm Hg in a 0.5-mm capillary), plus the much smaller readings resulting from the greater density of mercury as compared to 4-methyl-2-pentanone.

20.3 *Filter Paper*— Any high grade, medium-retention, nonashing cellulosic filter paper.

NOTE 15—Other porous filters such as sintered metal have been found to be satisfactory.

## 21. Calibration

21.1 **Warning**—Very low concentrations of mercury vapor in the air are known to be hazardous. Be sure to collect all spilled mercury in a closed container. Transfers of mercury should be made over a large plastic tray.

21.2 Place a column of clean mercury, approximately 70 mm (3 in.) long, in the capillary and measure its length with a cathetometer.

21.3 Transfer all of the mercury to a tared beaker and obtain the weight of the mercury on an analytical balance. Discard the mercury to be cleaned.

21.4 Since the density and weight of the column of mercury are known, its volume,  $V_M$ , in microlitres at room temperature (23°C), is given by the equation:

$$V_M = 10^3 \times W/13.54 \quad (3)$$

where:

$W$  = weight of the mercury, g, and  
13.54 g/mL = density of mercury at 23°C.

Since for a cylinder:

$$V_M = a_c l \quad (4)$$

where:

$a_c$  = cross-sectional area, mm<sup>2</sup>, and

$l$  = length of mercury column, mm, then:

$$a_c = V_M/l \quad (5)$$

21.5 Calibrations shall be made at 23°C.

21.6 See 11.2 for the use of NBS Standard Reference Material 1470 in checking the calibration of permeance-measuring apparatus.

## 22. Procedure

22.1 Center a piece of filter paper in the upper portion of the test cell.

22.2 Place the conditioned specimen smoothly on the upper portion of the test cell.

22.3 Lightly grease<sup>10</sup> the rubber gasket, O-ring, or flat metal that the surface of the specimen will contact. Avoid excessive grease.

22.4 Place the upper half of the cell on the base and clamp it firmly to achieve a tight seal.

22.5 Apply positive test gas pressure to both sides of the cell, flushing out all air before closing the outlet vent. A recommended flushing time is at least 10 min at a flow rate of about 100 mL/min.

NOTE 16—The pressure differential is obtained by monitoring and adjusting the gage pressure on the high-pressure side of the cell so that it is the desired amount above the observed barometric pressure on the open (downstream) side.

22.6 Introduce an approximately 20-mm liquid slug (keep it intact) at the top of the capillary (Note 17) and close the upper outlet vent after the slug rests on the bottom of the capillary (Note 18). The capillary shall be clean and free of obstructions.

NOTE 17—It is convenient to add the liquid slug to the capillary with a syringe fitted with a long thin needle to aid proper insertion.

NOTE 18—After lowering the liquid slug into the capillary, sufficient time must be allowed for drainage down the inner wall of the capillary before beginning to take a series of readings.

22.7 Adjust the pressure across the specimen to maintain the exact pressure differential desired.

22.8 Small leaks around connections and joints can often be detected with soap solutions, but in some cases it may be necessary to immerse the cell in water while applying gas pressure, in order to observe bubbles at leak sites. Small leaks occurring on the high-pressure side of the cell should not be considered significant.

22.9 After a time interval estimated to be sufficient for attaining steady-state, begin measuring the displacement of the slug, using a stop watch (or clock) and distance scale maintained on the capillary or cathetometer. Take measurements at the top of the meniscus.

22.10 On completion of the run, return the slug to its starting position by slightly opening the low-pressure vent.

22.11 Repeat the measurement as necessary to assure the attainment of a steady-state condition.

NOTE 19—The time required to reach steady state will depend upon the nature of the specimen, its thickness, and the applied pressure differential. For specimens of low permeability, changes in ambient pressure may

<sup>9</sup> A suitable dye is Victoria Blue B, or Sudan Red available from chemical supply houses such as Pfaltz and Bauer, Inc.

<sup>10</sup> Stopcock grease available from Dow Corning Corp. has been found suitable.

**TABLE 1 Results of Round-Robin Evaluation**

Material	Gas	$P$ (barrers) <sup>A</sup>	$P$ (Inch-pound units) <sup>B</sup>	( $S_r$ ) (barrers)	( $S_L$ ) (barrers)	( $CV_r$ ) (%)	( $CV_R$ ) (%)
Polyester film (100 A Mylar®)	O <sub>2</sub>	0.028	72.4	0.006	0.012	21	48
Polyester film (65 HS Mylar®)	O <sub>2</sub>	0.048	124	0.003	0.019	6	40
Polyester film (100 A Mylar®)	CO <sub>2</sub>	0.094	243	0.007	0.014	7	16
Polyester film (65 HS Mylar®)	CO <sub>2</sub>	0.18	466	0.009	0.028	5	16
Poly(propylene) film	O <sub>2</sub>	1.29	3340	0.15	0.28	12	25
Poly(ethylene) film	O <sub>2</sub>	1.94	5020	0.08	0.23	4	13
Poly(propylene) film	CO <sub>2</sub>	4.85	12550	0.45	0.69	9	17
Poly(ethylene) film	CO <sub>2</sub>	7.62	19710	0.40	0.94	5	13

( $S_r$ )<sub>*i*</sub> = the within-laboratory standard deviation of a single laboratory result for material *i*.

( $S_L$ )<sub>*i*</sub> = the square root of the between-laboratory component, of variance.

( $CV_r$ )<sub>*i*</sub> = 100 ( $S_r$ )<sub>*i*</sub> /  $P_r$

( $CV_R$ )<sub>*i*</sub> = 100[( $S_r$ )<sub>*i*</sub><sup>2</sup> + ( $S_L$ )<sub>*i*</sub><sup>2</sup>]<sup>1/2</sup> /  $P_r$

<sup>A</sup> One barrer equals 3.349 × 10<sup>-10</sup> m<sup>2</sup>·s·Pa (see Table X1.1)

<sup>B</sup> Inch-pound units are mL (STP) mil/m<sup>2</sup>·d·atm. See X1.1, X1.2, X1.3, and Appendix X2 for conversion factors.

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interfere, particularly if long periods of test and repeated measurements are required to obtain reliable results.

### 23. Calculation

23.1 Plot the capillary slug position versus elapsed time and draw the best straight line through the points so obtained.

23.2 Calculate the volume-flow rate,  $V_r$ , in microlitres per second of transmitted gas from the slope of this line as follows:

$$V_r = \text{slope} \times a_c \quad (6)$$

where:

slope = rate of rise of capillary slug, mm/s, and

$a_c$  = cross-sectional area of capillary, mm<sup>2</sup>.

23.3 Calculate the gas transmission rate (GTR) in SI units as follows:

$$\text{GTR} = 10^{-6} \times p_o \times V_r / (\text{ART}) \quad (7)$$

where:

$A$  = transmitting area of specimen, mm<sup>2</sup>,

$p_o$  = ambient pressure, Pa,

$R$  = universal gas constant ( $R = 8.3143 \times 10^{-3}$  L·Pa/(mol·K)), and

$T$  = ambient temperature, K.

23.4 Calculate the permeance,  $P$ , in SI units as follows:

$$P = \text{GTR} / (p - p_o) \quad (8)$$

where  $p$  is the upstream pressure in pascals.

23.5 A test result is defined as the value obtained from an individual determination of the permeance of a specimen.

NOTE 20—The reliability of the measurements can be assessed to some extent by making measurements on SRM 1470 (see 11.2).

### 24. Report

24.1 The report shall include the following:

24.1.1 Procedure used,

24.1.2 Description of the sample, including identification of composition, presence of wrinkles, bubbles, or other imperfections, and manufacturer, if known.

24.1.3 Test gas used, and test gas composition, including purity,

24.1.4 Test temperature in degrees Celsius, and the pressure difference used,

24.1.5 Each thickness measurement made plus the average for each specimen. When five or more thickness measurements are made per specimen, the average, standard deviation and number of measurements made may be reported instead of each measurement, and

24.1.6 Each measurement obtained plus the appropriate averages in the units of choice. When five or more replicates are obtained the average, standard deviation, and number of replicates may be substituted for the above.

### 25. Precision

25.1 *General*—An interlaboratory evaluation of this method has been conducted.<sup>11</sup> Ten laboratories participated in determining the permeability,  $P$ , of four materials to oxygen and carbon dioxide. The results from the round robin are summarized in Table 1. The results demonstrate clearly that the precision of the results obtained depends strongly, but in an unpredictable manner, on the combination of material and gas being tested. Potential users of this method must, therefore, use their own experience in assessing the precision of the results being obtained.

25.1.1 The contribution arising from the between-laboratory component of the variance is larger than that from the within-laboratory component for all materials. This indicates that there are systematic differences between the procedures used in different laboratories. The magnitudes of these differences must be determined whenever two laboratories are comparing results for referee purposes.

25.2 *Repeatability*—Approximately 95 % of all test results will lie within 2( $CV_r$ ) % of the mean of all test results obtained within a given laboratory on a given material. Typical values of ( $CV_r$ ) are given in Table 1.

25.3 *Reproducibility*—Approximately 95 % of all test results obtained in different laboratories will lie within 2( $CV_R$ ) %

<sup>11</sup> Supporting data are available from ASTM Headquarters. Request RR:D20-49.

**TABLE X1.1 Factors for Converting Permeabilities from One System of Units to Another**

Note 1—For instructions on using the table see X1.4.

Multiply ↓	To Obtain →	Unit System Dimensions of $P$			
		SI amol/m·s·Pa	Barrers 10 <sup>-10</sup> mL (STP) cm·s·cm Hg	Metric mL (STP) mil m <sup>2</sup> ·d·atm	Inch-pound mL (STP) mil 100 in. <sup>2</sup> ·d·atm
SI amol/m·s·Pa		1	2.986 × 10 <sup>-3</sup>	7.725	0.4984
Barrers 10 <sup>-10</sup> mL (STP) cm·s·cm Hg		0.3349 × 10 <sup>3</sup>	1	2.587 × 10 <sup>3</sup>	0.16691 × 10 <sup>3</sup>
Metric mL (STP) mil m <sup>2</sup> ·d·atm		0.12945	0.3865 × 10 <sup>-3</sup>	1	64.52 × 10 <sup>-3</sup>
Inch-pound mL (STP) mil 100 in. <sup>2</sup> ·d·atm		2.0064	5.991 × 10 <sup>-3</sup>	15.50	1

of the population mean of such values. Typical values of ( $CV_R$ ) for the material examined in the round robin are shown in Table 1.

25.4 Users who wish to test materials other than those considered in the round robin must make their own assessment

of the precision of their results. Variability between specimens is likely to be a dominant factor in such measurements.

## APPENDIXES

### (Nonmandatory Information)

#### X1. UNITS IN GAS TRANSMISSION MEASUREMENTS

X1.1 SI units for various quantities related to transmission of gases can be derived by recalling that the present standard defines the transmission rate,  $G$ , as the quantity of gas crossing a unit area of a barrier in unit time. Since the SI base unit for quantity of matter is the mole, the SI base unit for length is the metre, and the SI base unit for time is the second, the derived SI unit of transmission rate should be the mol/m<sup>2</sup>·s. Similarly, since the permeance,  $P$ , is defined as the ratio between the transmission rate and the partial pressure differential across the barrier, and since the SI unit of pressure is the pascal, appropriate SI units for permeances are mol/m<sup>2</sup>·s·Pa. Finally, for a homogeneous material, the permeability,  $P$ , is defined as the product of the permeance and the thickness of the film, which leads to the mol/m·s·Pa as the appropriate SI units.

X1.1.1 Appropriate unit prefixes must be attached to the SI units in order to bring the values that are actually observed onto a convenient scale for reporting or further manipulation. The following example will help to clarify this point: Consider a homogeneous film with a permeability of 1 amol/m·s·Pa (1 amol = 10<sup>-18</sup> mol) and a thickness of 25.4 m. The permeance of this film would be 39.37 fmol/m<sup>2</sup>·s·Pa (1 fmol = 10<sup>-15</sup> mol). If a pressure differential of one standard atmosphere (1 atm = 0.10132 MPa) were imposed across the barrier, the gas transmission rate would be 3.989 nmol/m<sup>2</sup>·s (1 nmol = 10<sup>-9</sup>

mol). Using the ideal gas law to convert this to inch-pound units yields a value of 7.725 mL(STP)/m<sup>2</sup>·d, which is a reasonable value for a good barrier.

X1.1.2 In these units the permeability of NBS Standard Reference Material to oxygen gas is approximately 7.8 amol/m·s·Pa.

X1.2 Table X1.1, Table X1.2, and Table X1.3 give conversion factors for converting measured permeabilities, permeances, and transmission rates between various unit systems. Considerable care must be taken in dealing with powers of 10 because transport coefficients can vary by as much as a factor of 10<sup>-5</sup> from one polymer to another.

X1.3 The major advantage of this proposed system of units over existing ones is that it essentially eliminates opportunities for incorrect dimensional calculations. It also affords a good basis for making comparisons when permeating substances are liquids or do not obey the ideal gas law. Modern coulometric and chromatographic detection systems are most readily calibrated in molar terms.

X1.4 In order to use the tables, proceed as follows: (1) label the measured quantity ( $G$ ,  $P$ , or  $P$ ) by  $X_i$ , where  $i$  is the number of the row in the table corresponding to the system of units in

**TABLE X1.2 Factors for Converting Permeances from One System of Units to Another**

NOTE 1—See X1.4 for instructions on using this table.

		Unit System Dimensions of $P$			
Multiply ↓	To Obtain →	SI $\text{fmol/m}^2 \cdot \text{s} \cdot \text{Pa}$	Barrer-type $10^{-10} \text{ mL (STP)} / \text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}$	Metric $\text{mL (STP)} / \text{m}^2 \cdot \text{d} \cdot \text{atm}$	Inch-pound $\text{mL (STP)} / 100 \text{ in}^2 \cdot \text{d} \cdot \text{atm}$
	SI $\text{fmol/m}^2 \cdot \text{s} \cdot \text{Pa}$	1	$29.86 \times 10^{-3}$	0.19621	$12.659 \times 10^{-3}$
	Barrer-type $10^{-10} \text{ mL (STP)} / \text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}$	33.49	1	6.571	0.4240
	Metric $\text{mL (STP)} / \text{m}^2 \cdot \text{d} \cdot \text{atm}$	5.097	0.15218	1	$64.52 \times 10^{-3}$
	Inch-pound $\text{mL (STP)} / 100 \text{ in}^2 \cdot \text{d} \cdot \text{atm}$	79.00	2.359	15.50	1

**TABLE X1.3 Factors for Converting Gas Transmission Rates from One System of Units to Another**

NOTE 1—See X1.4 for instructions on using this table.

		Unit System Dimensions of $G$			
Multiply ↓	To Obtain →	SI $\text{nmol/m}^2 \cdot \text{s}$	Barrer-type $10^{-10} \text{ mL (STP)} / \text{cm}^2 \cdot \text{s}$	Metric $\text{mL (STP)} / \text{m}^2 \cdot \text{d}$	Inch-pound $\text{mL (STP)} / 100 \text{ in}^2 \cdot \text{d}$
	SI $\text{nmol/m}^2 \cdot \text{s}$	1	22.414	1.9366	0.12494
	Barrer-type $10^{-10} \text{ mL (STP)} / \text{cm}^2 \cdot \text{s}$	$44.62 \times 10^{-3}$	1	$86.40 \times 10^{-3}$	$5.574 \times 10^{-3}$
	Metric $\text{mL (STP)} / \text{m}^2 \cdot \text{d}$	0.5164	11.574	1	$64.52 \times 10^{-3}$
	Inch-pound $\text{mL (STP)} / 100 \text{ in}^2 \cdot \text{d}$	8.004	179.40	15.50	1

which  $X$  was measured, (2) extract  $Y_j$  from the appropriate table as the value at the intersection of the  $i$ th row and the  $j$ th column where  $j$  labels the column corresponding to the units in

which  $X$  is to be expressed after conversion, and (3) obtain  $X_j$  from  $X_j = X_i Y_j$ .

## X2. ADDITIONAL CONVERSION FACTORS FOR VARIOUS PERMEABILITY UNITS

NOTE X2.1—To obtain unit in left-hand vertical column multiply unit in top horizontal column by figure opposite both units.

To Obtain	Multiply			
	$\frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}}$	$\frac{\text{cm}^3 \cdot \text{mil}}{\text{m}^2 \cdot 24 \text{ h} \cdot \text{atm}}$	$\frac{\text{cm}^3 \cdot \text{mil}}{100 \text{ in.}^2 \cdot 24 \text{ h} \cdot \text{atm}}$	$\frac{\text{cm}^3 \cdot \text{mm}}{\text{m}^2 \cdot 24 \text{ h} \cdot \text{atm}}$
$\frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}}$	1.00	$3.87 \times 10^{-14}$	$6.00 \times 10^{-13}$	$1.52 \times 10^{-12}$
$\frac{\text{cm}^3 \cdot \text{mil}}{\text{m}^2 \cdot 24 \text{ h} \cdot \text{atm}}$	$2.58 \times 10^{13}$	1.00	15.5	39.4
$\frac{\text{cm}^3 \cdot \text{mil}}{100 \text{ in.}^2 \cdot 24 \text{ h} \cdot \text{atm}}$	$1.67 \times 10^{12}$	$6.45 \times 10^{-2}$	1.00	2.54
$\frac{\text{cm}^3 \cdot \text{mm}}{\text{m}^2 \cdot 24 \text{ h} \cdot \text{atm}}$	$6.57 \times 10^{11}$	$2.54 \times 10^{-2}$	0.394	1.00

### X3. DERIVATION OF EQUATION FOR PERMEANCE USING THE MANOMETRIC GAS CELL

X3.1 The following symbols are used in the derivations of the equation used in Section 13 to calculate the permeance.

- $a$  = area of capillary  $\overline{AB}$ ,  $\text{mm}^2$ ,
- $A$  = area of transmission,  $\text{mm}^2$ ,
- $dP$  =  $dh$  = differential pressure change of transmitted gas, mm Hg,
- $dV$  =  $ad h$  = differential volume change of transmitted gas,  $\mu\text{L}$ ,
- $h_o$  = initial height of mercury in the capillary leg at the start of the actual transmission run with steady-state conditions attained, mm,
- $h$  = height of mercury in cell capillary leg at any given time, mm,
- $h_B$  = maximum height of mercury in the cell manometer leg from the datum plane to upper calibration line B, mm,
- $h_L$  = height of mercury in cell reservoir leg from datum plane to top of mercury meniscus, mm,
- $n_o$  = quantity of gas transmitted at the start of the actual transmission run after steady-state conditions have been attained, mol,
- $n$  = quantity of gas transmitted, at any given time, mol,
- $P$  = permeance of the film, the SI unit of permeance is  $1 \text{ mol} (\text{m}^2 \cdot \text{s} \cdot \text{Pa})$ ,
- $p_t$  =  $(h_L - h)$  = pressure of transmitted gas at time  $t$ , mm Hg,
- $p_u$  = pressure of gas to be transmitted, mm Hg,
- $R$  = universal gas constant,  $8.314 \times 10^3, \text{ L} \cdot \text{Pa}/(\text{mol} \cdot \text{K})$ ,
- $t$  = time, h,
- $t_o$  = time at start of the actual transmission run after steady-state conditions have been attained, h,
- $T$  = absolute temperature, K,
- $V_{BC}$  = volume from B to C,  $\mu\text{L}$ ,
- $V_{CD}$  = void volume of depression,  $\mu\text{L}$ ,
- $V_f$  =  $(V_{BC} + V_{CD})$ ,  $\mu\text{L}$ , and
- $V_t$  =  $[V_f + a(h_B - h)]$  = volume of transmitted gas,  $\mu\text{L}$  at time  $t$ .

X3.2 The number of mols of gas transmitted,  $n$ , may be determined from the ideal gas law (which is valid at the low pressure involved) as follows:

$$n = p_t V_t / RT \quad (\text{X3.1})$$

For differential changes in  $p_t$  and  $V_t$  Eq X3.1 can be differentiated as follows:

$$\begin{aligned} nRT &= p_t V_t \\ RTdn &= d(p_t V_t) \end{aligned} \quad (\text{X3.2})$$

$$RTdn = p_t dV + V_t dp \quad (\text{Note X3.1})$$

NOTE X3.1—This differentiation is the form  $d(uv) = udv + vd u$ . Substitute into Eq X3.2 the values for  $dV$  and  $dP$  given in the definition of symbols.

$$\begin{aligned} RTdn &= -p_t adh - V_t dh, \text{ or} \\ dn &= (-ap_t dh - V_t dh)/RT \end{aligned} \quad (\text{X3.3})$$

By definition,

$$\begin{aligned} p_t &= (h_L - h), \text{ and} \\ V_t &= [V_f + a(h_B - h)] \end{aligned}$$

Therefore, substituting into Eq X3.3 and collecting terms,

$$\begin{aligned} dn &= \{-a(h_L - h)dh - [V_f + a(h_B - h)]dh\}/RT \\ dn &= [(-ah_L + ah)dh - (V_f + ah_B - ah)dh]/RT \\ dn &= [dh(-ah_L + ah - V_f - ah_B + ah)]/RT \\ dn &= \{dh[2ah - a(h_L + h_B) - V_f]\}/RT \end{aligned} \quad (\text{X3.4})$$

X3.3 The permeance ( $P$ ) expressed in  $\text{cm}^3/\text{m}^2 \cdot 24 \text{ h} \cdot \text{atm}$  can be obtained by integrating Eq X3.4 and using the following conversion factors:

$$\begin{aligned} \int_{t_o}^t P dt &= \int_{n_o}^n dn \text{ mol} \times \frac{24}{24 h} \\ &\times 22 \ 415 \frac{\text{cm}^3}{\text{mol}} \times \frac{760 \frac{\text{mm}}{\text{atm}} \times 10 \ 000 \frac{\text{cm}^2}{\text{m}^2}}{P_d(\text{mm}) \times A(\text{mm}^2)} \end{aligned}$$

The term  $P_d$ , which is the driving force, and  $A$ , the area of transmission, must be included in this equation in order to

obtain the permeance in the desired units. Collecting terms and substituting for the following:

$$P_d = (p_u - p_i)$$

$$\int_{t_0}^t dt = \int_{p_i}^{p_u} \frac{dn}{(p_u - p_i)A} (24 \times 22\,415 \times 760 \times 10\,000)$$

or substituting for  $dn$  from Eq X3.4 and  $p_i = (h_L - h)$ :

$$\int_{t_0}^t P dt = \frac{1}{ART} \int_{h_0}^h \frac{[2ah - a(h_L + h_B) - V_f]dh}{p_u - (h_L - h)} \quad (\text{X3.5})$$

X3.4 To find an expression that applies over an extended period of time, Eq X3.5 must be integrated as described by Evans.<sup>12</sup>

$$\int_{t_0}^t P dt = \frac{1}{ART} \left[ 2a \int_{h_0}^h \frac{h dh}{p_u - (h_L - h)} - a(h_L + h_B) \int_{h_0}^h \frac{dh}{p_u - (h_L - h)} - V_f \int_{h_0}^h \frac{dh}{p_u - (h_L - h)} \right]$$

The first term can be integrated by parts or found in standard integration tables. The remaining terms are straightforward. The following result is obtained for steady-state gas transmission:

$$P(t - t_0) = \frac{-1}{ART} \left\{ 2a(h_0 - h) + [V_f + a(2p_u - h_L + h_B)] \ln \left[ \frac{p_u - (h_L - h)}{p_u - (h_L - h_0)} \right] \right\}$$

This can be written in the form:

$$P(t - t_0) = \frac{-1}{ART} \left\{ 2a(h_0 - h) + [V_f + a(2p_u - h_L + h_B)] \ln \left[ 1 - \frac{(h_0 - h)}{S} \right] \right\} \quad (\text{X3.6})$$

<sup>12</sup> Evans, R. E. "The Calculation of Gas Transmission Rates Using Manometric Methods", *Journal of Testing and Evaluation*, ASTM, Vol 2, No. 6, pp. 529-532.

where:

$$S = p_u - (h_L - h_0).$$

Eq X3.6 is the exact relationship for calculating steady-state permeance over an extended period of time.

X3.5 If we assume that time-lag effects are not important, Eq X3.6 takes proper account of the fact that the driving force for permeation is decreasing continuously during a manometric permeation experiment. If one assumes that the rate of pressure rise is constant with time in the downstream cell volume, thereby failing to correct for the decrease in driving force, the resulting permeance values are too low. If we denote the permeance value obtained from uncorrected data by  $P'$ , we can say that the true permeance,  $P$ , is given by

$$P = \frac{P'}{1 - \epsilon}$$

X3.6 It can be demonstrated, by computer simulation or by series expansion methods, that

$$\epsilon = (h_L - h_p) \left[ \frac{a}{V_f + a(h_B - h_L)} + \frac{1}{2p_u} \right] \text{ for } \epsilon < 0.3$$

where  $h_p$  is the depression of the mercury column at the end of the experiment. Evans has demonstrated<sup>12</sup> that  $\epsilon$  can become as large as 0.2 in realistic situations.

X3.7 If the function  $g(h)$ , as given by the right-hand side of Eq X3.6, exhibits curvature when plotted as a function of time one or more of the assumptions used in deriving Eq X3.6 is not being met, and further studies are needed to establish the causes of this behavior.

X3.7.1 Possible sources of error include (1) failure to achieve steady-state conditions, (2) the presence of time-lag effects, and (3) viscoelastic processes.

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